21. "Black nitrogen" – its impact on size and quality of the refractory soil organic N and C pool

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Organic nitrogen represents an integral part of litter and humic material in which it occurs mainly in peptideous forms. During vegetation fires, it is incorporated into charred residues, which are highly resistant to further degradation. Thus, this nitrogen is expected to be efficiently sequestered from the global elemental cycle. Considering that during vegetation fires in particular N-containing litter and humic material are affected, it is clear that charred organic N must play an important role within the soil organic matter (SOM) stabilization processes of most fire-affected regions. On the other hand, in "Black Carbon" (BC) models, this organic N is commonly neglected, which is the reason why up to now, only limited knowledge is available concerning its structure, its recalcitrance or its persistence and turnover rate in soil systems. Nevertheless, exactly this knowledge is needed, if we seek for a better understanding of the impact of fires on the global biogeochemical cycles. As a first step in this direction, the chemical alterations during BN were studied by charring casein as a model protein under controlled conditions. Aproximately 62% of its C and 46% of its N survived exposure to 350°C for 8 min demonstrating a relatively high resistance of proteins against thermal breakdown. Increasing the temperature to 450°C reduced the C and N recoveries to 29% and 23%, respectively.

Solid-state ^{13}C and ^{15}N NMR spectroscopy identified the charred N structures mostly as pyrrole/indole-type N with minor contribution of pyridine N. None of those structures were observed in higher amounts in SOM modified solely by microorganisms, but were also detected in soils with fire history. Combining NMR spectroscopy and elemental analysis, the contribution of such pyrogenic N-heterocyclic C to the total organic C of biochars derived from grass residues and peat were calculated to be more than 50% and 12%, respectively. Applying the same approach to a soil that was affected by a wild-fire one year before sampling identified 27% of BC and 8% of its total C as pyrogenic N-heterocyclic C. Increasing the recovery time to 24 years had no major impact on those numbers, which is in accordance with the high recalcitrance of this material. With these simple calculations, we were able to clearly demonstrate that BN survives pedogenetic processes at least on a medium term, which underlines its relevance within the geobiochemical cylces and its important role for determining the potential of soils as a N- and C-sink.